THESIS

The Rate of Oxidation of Lime-Sulphur Solutions

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1. INTRODUCTION

Among the insecticides, lime-sulphur is one of growing
importance. Already it has found extensive use as a spray on
all kinds of fruit trees, shrubs and vines and is also largely
employed as an animal dip for scab diseases, and for the ex-
termination of lice in hen houses. It is especially adapted
for the destruction of soft-bodied scale insects on fruit
trees, such as the San Jose Scale.

Since lime-sulphur has proved of value in controlling
these insects, an addition to the meagre knowledge of the
action of the constituents and of their properties which are
responsible for the destruction of the scale insects would be
of material value in increasing the efficiency of the lime-
sulphur. Already the work done on determining the exact con-
stituents of lime-sulphur has been very extensive, so that at
present its composition is fairly well established. The prob-
lem which I have undertaken deals with the oxidizing power of
lime-sulphur. The specific object of the thesis is to deter-
mine the rate of oxidation of lime-sulphur solutions of

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different concentrations and under varying conditions.

2. REVIEW OF LITERATURE

The literature on the subject of lime-sulphur solutions
has now become quite extensive, but has dealt for the most
part with the chemical composition of lime-sulphur, or its
fungicidal and insecticidal value. The work of the early in-
vestigators was handicapped to a great extent by limitations
in their methods of analysis. Quite recently, Chapin (1 & 2)
developed some new methods, which allow an exact knowledge of
the constituents of lime-sulphur compounds. The advantage of
these methods lies in the fact that they are all volumetric,
and can be carried out quite rapidly, giving accurate results,
which cannot be said of the former methods. Since these methods
as given by Chapin (1 & 2) are scattered through various arti-
cles and bulletins, a detailed description of them, has been in-
troduced later on in this thesis.

The first investigator to point out the real constituents
of the spray solution was Haywood (4) in the year 1901. He
showed that the spray contained considerable amounts of poly-
sulphides, and thiosulphate, but smaller quantities of sulphate
and sulphite. He thought that a small amount of calcium hydrox-
ide might be present. From the analyses which he made these
conclusions were drawn:

1. That a one hour period of boiling dissolves practically
all of the sulphur.

2. That the thiosulphates are somewhat increased by a more pro-

longed period of boiling.

3.   That the sulphate and sulphite are also increased when
the period of boiling is greater than one hour.

Haywood believed that the primary reaction between lime and
sulphur was as follows:

   (1) $3Ca(OH)_2$ plus $12S = CaS_2 O_3$ plus $2CaS_5$ plus $3H_2O$
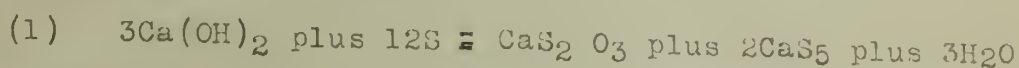
However, he also noticed that this reaction would lead to the
formation of less sulphur as thiosulphate and more sulphur as
pentasulphide than was indicated in his results. Therefore,
he came to the conclusion that this secondary reaction took
place:

   (2) CaS_5 plus $3O = CaS_2 O_3$ plus $3S$
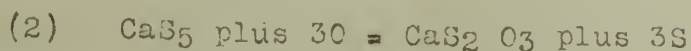
i.e. The calcium pentasulphide is partially changed to calcium
thiosulphate and free sulphur. Then this sulphur which is set
free combines to a large extent with calcium hydroxide accord-
ing to equation (1).   Therefore, if the boiling were continued,
it seems logical that more thiosulphate would continually be
formed at the expense of the pentasulphide.   In the next place,
it is a well known fact that thiosulphates in solution change
slowly to sulphite, which in turn changes to sulphate: as,

   (3) $CaS_2O_3 = CaSO_3$ plus S

   (4) $CaSO_3$ plus $O = CaSO_4$
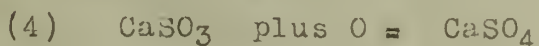
All of the above reactions are well known, and all but the first
verified by other investigators.

      Considerable work on the composition of lime-sulphur was
also done at the New York State Experiment Station in 1909 by
Van Slyke, Hedges, and Bosworth (7). The results which they

obtained concerning the preparation, amount of ingredients, products formed and time of boiling were similar to previous work.

Haywood (4) was also one of the first investigators to carry out any definite systematic field experiments to show the relative insecticidal and fungicidal value of the constituents. He attempted to study the decomposition of the spray by experiments approximating as nearly as possible the conditions of the spray on the tree. Different samples were sprayed on filter papers, and put in porcelain dishes out of doors in the sunlight for various lengths of time. Some were moistened each morning to represent dew. From these experiments he found that the principal immediate products of decomposition were calcium thiosulphate and free sulphur, and that the thiosulphate gradually decomposed to form sulphite and liberate more sulphur, and finally the calcium sulphite was oxidized to sulphate.

Tarter and Bradley (6) of the Oregon Experiment Station perfected methods for the determination of the various forms of sulphur. These methods, in the writer's opinion, are not as accurate and decisive as Chapin's newer volumetric methods.

Certain terms introduced by Tartar and Bradley to differentiate the two kinds of sulphides in lime-sulphur, need a word of explanation. For instance, the sulphur equivalent to form the monosulphide is generally spoken of as "sulphide" sulphur, and the remainder as "polysulphide" sulphur. Thus, when the amount of "sulphide" sulphur and "polysulphide" sulphur is known the simplest formula for the polysulphide can be readily calcu-

lated. Formerly, it was believed that the polysulphides exist-
ed entirely as the pentasulphides. But if that were the case,
the amount of "polysulphide" sulphur would be exactly four
times that of the "sulphides" sulphur, and in the results of
Tartar and Bradley (6), the "polysulphide" sulphur was approx-
imately three and one-half times the amount of the "sulphide"
sulphur. This showed that the polysulphides in solution are
probably not one compound alone but a mixture of the tetra and
pentasulphides of calcium.

Chapin (3) states that all lime-sulphur solutions are sub-
ject to hydrolytic decomposition according to this equation:

$$CaS_x \text{ plus } H_2O \rightleftharpoons Ca(OH)_2 \text{ plus } H_2S \text{ plus } (X-1)S$$
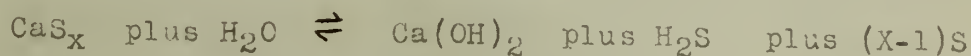
The pressure of the reaction from left to right increases with
the rise of temperature. Then the calcium hydroxide and sul-
phur are supposed to react according to the equation:

$$3Ca(OH)_2 \text{ plus } 12S = CaS_2O_3 \text{ plus } 3H_2O \text{ plus } 2CaS_x$$

Hence the final hydrolysis would be represented as follows:

$$CaS_5 \text{ plus } 3H_2O = CaS_2O_3 \text{ plus } 3H_2S$$

Chapin (1 & 2) says that the lime-sulphur solutions may be
either basic (contain free $Ca(OH)_2$ or calcium hydrosulphides)
or acidic (free H_2S or calcium hydrosulphides) according to the
degree of hydrolysis, which is regulated by the temperature and
the time the material has stood. Most solutions, after a few
weeks standing, are acidic.

Vermorel and Dantony (8) have shown that at ordinary tem-
perature, oxysulphides of calcium, CaS_2O_3 and a little CaS_4

are formed after standing several months. During the preparation of the material up to 100 degrees C., there was an increase in the soluble salts formed. Sulphides predominate at high temperatures, while CaS_2O_3 is chiefly formed at low temperatures. The greatest amount of sulphur dissolved, increases during the first forty-five minutes of boiling, and after that time there is a decrease. Tetra-sulphide is first formed and then pentasulphide. This agrees with the work of Tartar and Bradley (6) particularly in the preliminary formation of CaS_4 and the subsequent formation of CaS_5. The greatest amount of sulphur is dissolved when the ingredients are used in the proportion of 3.2 parts of sulphur to 1 part of lime. If the solution is cooled slowly, there is less CaS_2O_3, while the greater the surface exposed to the air the more CaS_2O_3. Excess of lime in the sediment tends to the formation of oxysulphides of calcium. The authors also state that the density of the lime-sulphur is no basis on which to estimate the amount of sulphur present.

The principal work done on determining the properties of lime-sulphur which make it effective in killing scale insects was done by Shafer (5). The following is a brief summary of his work. He showed that when large insects having heavy chitinous walls are treated with lime-sulphur, it seemed to have little effect. Large tomato worms were not killed after being submerged for two minutes in the solution. They showed some irritation for a time, but this wore off and in most cases there was no apparent permanent irritation. With delicate insects

with thin chitin, irritation was greater and when the solution
was applied to a small portion of the delicate body-wall, that
part might be killed before the rest of the body. There was no
means of proving satisfactorily that the lime-sulphur wash had
penetrated into the body-tissue.

It has been observed that on sunny days an odor similar to
that of sulphur dioxide was apparent in orchards sprayed with
lime-sulphur. As small amounts of this gas can bring about
torpor and death to insects, experiments were conducted to de-
termine whether sulphur dioxide was given off on surfaces spray-
ed with this wash. Paper and twigs were sprayed, and confined
in a container that could be exposed to strong sunlight for
various lengths of time. Air thus confined was tested for sul-
phur dioxide by passing it through a solution of iodine with
starch paper. No trace of sulphur dioxide was found in any
case. Other experiments tend to show that sulphur dioxide would
not be formed unless the temperature was much higher than under
the conditions in the orchard. It was noticed, however, in these
experiments that the volume of air was decreased. Hence, the
question arose, could it be possible that oxygen was used in such
amounts as to partially or wholly deprive the insect beneath
the scale-covering of that gas.

A study was made by Shafer to see whether the bodies of
the insects rendered comatose (i.e. unable to move until after
being exposed to fresh air) had really all been wet with the
spray. His results indicated that many of the bodies of the in-
sects had not been wet with the insecticide. This fact added

weight to the suspicion that some of the treated insects might be comatose from lack of oxygen. It was found that the insecticide was apt to stick especially well around the margin of the scale, and where the scale was in contact with the plant surface. After some time in contact with the scale, the lime-sulphur around the margin tended to soften the recently secretad wax.

The next thing determined was to see just how long the San Jose Scale insects could be without oxygen and still recover. It had been found that small insects, like plant lice used relatively much more oxygen than larger insects. The scales were placed on small blocks of apple to serve as food. These were placed in containers of pure nitrogen, above mercury for definite periods of time, some were kept in the air to serve as checks. Those over nitrogen were then removed to the air. After about forty-eight hours they were examined to see if any were alive. Of those kept in the nitrogen for eighteen hours almost all were dead. Several were alive at the end of fourteen to fifteen hour periods. Fourteen hours after the treatment with lime-sulphur, many scale insects were more or less comatose than at first, but revived somewhat after a few minutes in fresh air. They would onntract after a while upon being pricked with a needle point. They revived more quickly than specimens that had been kept in pure nitrogen for fourteen hours.

After carrying out complicated experiments on apple trees, Shafer (5), believed that the limited air space about

a scale insect must tend to become deficient in oxygen from three causes:

(1)   The tree on one side is using oxygen and giving off carbon dioxide.

(2)   The waxy scale covering coated with lime-sulphur seals the scale to the tree.

(3)   The insect itself uses oxygen and gives off carbon dioxide.

Shafer states that this is not absolute proof that the insect becomes comatose from lack of sufficient oxygen, but is general evidence that it may be the case.

Wallace, Blodgett, and Hesler (9) at the Cornell Station also did work on the fungicidal value of lime-sulphur. They sprayed glass sides, and subjected them to atmospheric conditions. Drops of water containing fungus spores were placed on the slides. The number of spores germination on the slides was used as a criterion. Their results showed, that lime-sulphur of a strength safe for foliage was only fairly effective as a fungicide.

3.   EXPERIMENTAL WORK

Storage

Commercial lime-sulphur, obtained from the Bowker Insecticide Company, Boston, Massachusetts, was used in the experimental work which follows. It was absolutely necessary to find a satisfactory method of storage in order to exclude air from the material. A 2-3 liter bottle with an outlet tube at the bottom was employed. The outlet at the bottom consisted

of a cork stopper with a hole in it containing a bent glass
tube with a glass stop-cock. About an inch of turbine oil
was poured on the top of the liquid to exclude air, and the
bottle loosely stoppered with just sufficient inlet to allow
the liquid to be drawn off.

Analysis

(a) Solutions Required

Chapin's volumetric methods of analysis were adopted be-
cause of their superiority. They are all titration methods us
ing N/10 solutions and 10cc. of the lime-sulphur. The solu-
tions required for the complete analysis are as follows:

(1) N/10 HCl

(2) N/10 NaOH

(3) N/10 Iodine

(4) N/10 Sodium thiosulphate

(5) 10% solution of NH_4 Cl

(6) Methyl red indicator (0.2% in alcohol)

(7) Starch solution

(8) Ammonical zinc chloride (a) Dissolve 6.5 grams
     of C. P. metal in some excess of HCl diluting to
     about 900 cc. and adding sufficient concentrated
     ammonia to obtain a clear solution and then di-
     lute to 1000 cc; or (b) dissolve 50 grams of
     pure zinc chloride in water, and add concentrat-
     ed ammonia in sufficient quantity to redissolve
     the precipitation first formed.

(9) 10% solution of C.P. anhydrous sodium sulphite
     (recently prepared).

(10) 10% solution of crystallized strontium chloride

(11) 10% solution of crystallized disodium phos-
     phate.

(12) 10% solution of tartaric acid

(b) Definitions

In order to understand the analysis definitions of the
terms introduced by Chapin are required:

<u>Sulphide-base figure:</u> represents the cc. of N/10 base present
in 10cc. of solution whether existing as free lime or the var-
ious possible calcium sulphides. Calculations from this figure
lead to the amounts of monosulphur i.e. the amount of sulphur
as CaS.

<u>Reaction figure:</u> represents the cc. of N/10 base or acid
(H_2S) present in 10 cc. of solution in excess of the quantity
necessary to form neutral salts of the formula CaS_x. The re-
action figure has a plus sign if there is excess base; if there
is excess acid, a negative sign.

<u>Sulphide-acid figure:</u> represents the cc. of N/10 acid (H_2S_x)
present in 10 cc. of the solution whether existing free or as
various possible calcium sulphides.

(c) Calculations

The calculations of the various forms of sulphur exist-
ing in the diluted lime-sulphur are obtained by the following
formulae:

Sulphide-acid figure times 0.0016035 times 10 = % monosulphur

 Poly-sulphide figure   "   0.003207   "   10 = % poly-sulphur

Thiosulphate figure times 0.006414 times 10 = % thio-sulphur

Algebraic addition of the sulphide-acid figure and the reaction figure = the sulphide-base figure.

(d) Order of Analysis

The determinations should be made in this order:

1. Sulphur as thiosulphates

2. Reaction figure

3. Sulphide-acid figure

4. Mono-sulphide sulphur

5. Sulphide-base figure

6. Polysulphide-sulphur

(e) Description of the Methods of Analysis

<u>Thiosulphates</u>: The principle of the determination consists in removing all the sulphur as ZnS with ammonical zinc chloride. The ZnS is then filtered off, the filtrate made slightly acid with tartaric acid, and the thiosulphate in the filtrate titrated with iodine. In detail, about 20 cc. of the ammonical zinc chloride is used with 10 cc. of the diluted sample. The mixture is heated on the steam bath for thirty minutes with occasional stirring, filtered and the precipitate washed with hot water. The filtrate is cooled, one gram of C.P. KI added, followed by methyl red indicator, and the filtrate is cautiously rendered slightly acid with 10% tartaric acid, finally titrating with iodine. The number of cc. of iodine used is equal to the thiosulphate figure. From this, the per cent of thiosulphate is obtained by multiplying by 0.006414 and by 10.

Reaction figure: To determine the reaction figure, a nearly
neutral solution of sodium tetrathionate is prepared as follows:
Into a 300 cc Erlenmeyer flask run about 25% excess of N/10
iodine solution, which must be more than the amount of N/10 HCl
necessary to precipitate all the sulphur. Add N/10 Na₂S₂O₃
until the color of iodine is nearly discharged, then a little
N/10 HCl to destroy any iodates and just completely decolorize
with thiosulphate solution. Add two drops of methyl red and
titrate with N/10 NaOH to alkalinity, and then add sufficient.
acid to bring back to faint acidity. Ten cc. of the alkali are
now put in, followed by 5 cc. of 10% NH₄Cl solution, and final-
ly 10 cc. of the diluted lime-sulphur solution. The solution
is allowed to stand three minutes, and then titrated with N/10
HCl to a distinct end point. Determine the equivalent of 10
cc. of N/10 alkali in terms of N/10 acid and algebraically sub-
tract it from the actual titration which gives the "reaction
figure".

The action of the iodine on the thiosulphate forms tetra-
thionate. The NH₄ Cl reduces the OH ions formed from the NaOH
to a desirable concentration. Upon the addition of the lime-sul-
phur of the CaSₓ reacts with the tetrathionate to form two mole-
cules of thiosulphate. Bringing the solution back to neutral-
ity with acid or base determines the amounts of basic or acidic
material which entered the system with the lime-sulphur. The
reaction of the tetrathionate with the monosulphur is as follows:

$$CaS \text{ plus } Na_2S_4O_6 = CaS_2O_3 \text{ plus } Na_2S_2O_3 \text{ plus } S.$$
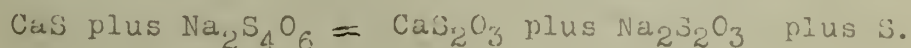
For every atom of monosulphur in the solution there are two thiosulphate molecules formed.

<u>Sulphide-acid figure:</u> To the liquid from the "reaction figure", iodine solution is added until it affects starch solution. Thus the iodine reacts with the thiosulphate (formed as in the above reaction) as follows:

$$2Na_2S_2O_3 \text{ plus } I_2 = Na_2S_4O_6 \text{ plus } 2NaI$$

$$2CaS_2O_3 \text{ plus } I_2 = CaS_4O_6 \text{ plus } CaI_2$$

From the resulting total iodine titration must be substracted the thiosulphate titration, and the remainder will be the "sulphide-acid figure."

<u>Per cent Mono-Sulphur:</u> Sulphide-acid figure times 0.0016035 times 10.

<u>Sulphide-base figure:</u> Algebraic addition of the "sulphide-acid figure" and the "reaction figure".

<u>Polysulphide Sulphur:</u> The method is based on the following reaction:

$$Na_2SO_3 \text{ plus } S = Na_2S_2O_3$$
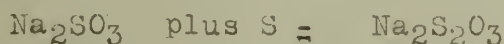
Into a mixture of 10 cc of a recently prepared 10% solution of C.P. Na_2SO_3 and 20 cc. of N/5 ammonical $ZnCl_2$, pipette 10 cc. of a diluted sample containing 1.5 -2% sulphide sulphur. Insoluble zinc sulphide and free sulphur are formed, the free sulphur being immediately taken up by the $Na_2 SO_3$.

$$CaS_x \text{ plus } ZnCl_2 = CaCl_2 \text{ plus } ZnS \text{ plus } S(x-1)$$

The mixture is placed on a steam bath at full heat for forty-five minutes and shaken at ten minutes. Then 20 cc. of a 10%

SrCl$_2$ solution is added to remove the excess sulphite which would interfere later.
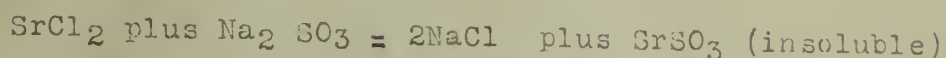
SrCl$_2$ plus Na$_2$SO$_3$ = 2NaCl plus SrSO$_3$ (insoluble)
Filter and catch the filtrate in a 250 cc. volumetric flask, washing the precipitate with hot water. Cool the liquid, add to it 0.5 -1.0 cc. of 10% disodium phosphate and make up to the mark. Shake, filter the liquid through a dry filter paper, and throw away the first 25 cc. of filtrate. Of this solution, 200 cc. of the solution are to be used. The phosphate solution removes the last traces of the sulphite. After methyl red indicator is added, make the liquid slightly acid with 10% tartaric acid solution. Titrate with N/10 iodine after the addition of starch. For every atom of polysulphide, one molecule of Na$_2$S$_2$O$_3$ has been formed which can be measured with iodine. From the cc. of iodine used, the cc. of thiosulphite originally present should be subtracted. In completing the calculation, bear in mind that only 200 cc., or four-fifths of the solution were used in the final titration. The number of cc. of iodine used is equal to the polysulphide figure. From this, the per cent of polysulphide sulphur is obtained by multiplying by 0.003207 and by 10.

(f) Results of Analysis

(Sample from Bowker Insecticide Co.)

The results of the analysis carried out according to the above procedure may be seen in the following table.

Specific Gravity	Thiosulphate Figure	Per cent Thiosulphate Sulphur	Reaction Figure	Sulphide acid Figure	Sulphur base Figure	Per cent Monosulphide Sulphur	Polysulphide Figure	Per cent Polysulphide Sulphur
1.31 or 34Be	4.34	2.78	-0.53	43.40	42.87	6.96	79.16	25.39

Total Sulphide Sulphur ∪ Per cent	Per cent Total Sulphur	Total Equivalent CaO*	Analytical Ratio $\frac{Total\ CaO}{Total\ S}$	Value of X in CaSx
32.35	35.13	14.89	0.424	4.65

* Estimated by calculation from the results for the various
forms of sulphur.

The analysis showed that the material was satisfactory
for performing oxidation experiments. Although the per cent
mono-sulphide sulphur is quite large, the polysulphide sulphur
is also relatively high, being 4.65 times that of the mono-
sulphide sulphur. This relationship is shown in the column
labelled "value of X in CaS_X". The value 4.65 is obtained by
dividing the total sulphide-sulphur by the mono-sulphide sul-
phur, and hence the symbol of this limesulphur might be written
$CaS_{4.65}$. Assuming that the polysulphides in the lime-sulphur
are only CaS_4 and CaS_5, it would consist of molecules of CaS_4
and CaS_5 in the ratio of 35: 65. The fact that the solution
had a negative reaction figure is explained by Chapin (3) as
follows:

$$CaS_X \text{ plus } 2H_2O = Ca(OH)_2 \text{ plus } H_2S \text{ plus } (x-1)S$$
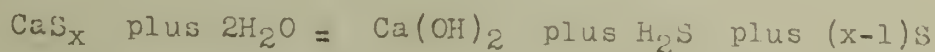
Lime-sulphur solutions when stored undergo the hydrolysis shown
in the above equation. The reaction proceeds until inhibited
by the accumulation of hydrogen sulphide unless the latter is
allowed to escape. The free calcium hydroxide produced, reacts
with free sulphur or polysulphur, and is thus removed from the
sphere of action. The remaining hydrogen sulphide is respon-
sible for the negative reaction of the lime-sulphur solution.

Preliminary Experiments

A few rough preliminary tests were first made in order to
get some idea how quickly and to what extent the oxygen in the
air was absorbed by lime-sulphur. To determine this, a graduat-
ed tube (50 cc.) about 1 cm. in diameter and closed at one end
was used. The lime-sulphur was diluted as for the San Jose Scale

spray (one part of lime-sulphur to eight parts of water.) and 20 to 25 cc. introduced into the tube. The volume of air above the lime-sulphur was noted, and then the tube was corked and shaken for different intervals of time, removing the cork each time under the lime-sulphur solution and noting the rise of the liquid in the tube, due to the absorption of oxygen. In this way, it was soon observed that the bulk of the oxygen was absorbed during the first eight or ten minutes, and the rest at a gradually decreasing rate until practically all the oxygen had been absorbed. Another graduated tube, about 1 cm. in diameter was filled with air and inverted over the diluted (1 to 8) lime-sulphur solution. The lime-sulphur gradually rose in the tube until in about two days, the entire amount of oxygen in the tube had been absorbed. Obviously, the time would have been much shorter if the surface had been distrubed by shaking.

After performing these preliminary tests, it was evident that the rate of oxidation could be determined easily, if air could be exposed to the lime-sulphur for short, definite periods of time, and then removed, and the oxygen absorbed, measured. Such a method would do away with the tedious analytical processes which would be involved in determining the changes brought about in various samples of lime-sulphur by different degrees of oxidation.

Apparatus

The apparatus finally decided upon was that which is used in ordinary gas analysis. This consisted of a gas burette and an absorption pipette. A drawing of the apparatus has been made

on the following page. The gas burette is made up of two
glass tubes set in wooden stands. The tubes are bent at
right angles at the bottom, and are drawn out so as to afford
convenient attachments for the rubber tube which joins them.
The measuring tube (a) ends in a capillary tube (c) over which
a short piece of rubber tubing may be slipped. A pinch cock
(d) is placed on this rubber tube. The tube is graduated in
cubic centimeters (up to 100 cc.). It is connected to the ab-
sorption pipette by means of a glass capillary tube (f). The
second tube (b) is called the leveling tube and serves to hold
the confining liquid. For the absorption apparatus, a double
pipette was employed. The absorbing reagent, or in this case,
the lime-sulphur, is placed in bulb (g) and when this bulb is
filled with gas, the liquid is forced into bulb (h). Bulbs
(i) and (j) are connected to (g) and (h) by a rubber tubing,
and the bulb (i) filled with pyrogallic acid in order to absorb
oxygen from the air in (h) and to keep oxygen out of (g) and
(h). When bulb (g) had to be refilled with a new solution of
lime-sulphur, bulbs (i) and (j) were pinched off at (e) and
disconnected. This facilitated the filling of bulbs(g), which
had to take place often in order to study the rate of oxidation
under various concentrations and under different temperatures.

Part I. Experiments with Air at a Minimum

A. Concentrations of Lime-Sulphur Varied.

In the first series of experiments which were carried out,
the concentration of the lime-sulphur solutions was varied;
that is, the various dilutions were taken and exposed to a limit-
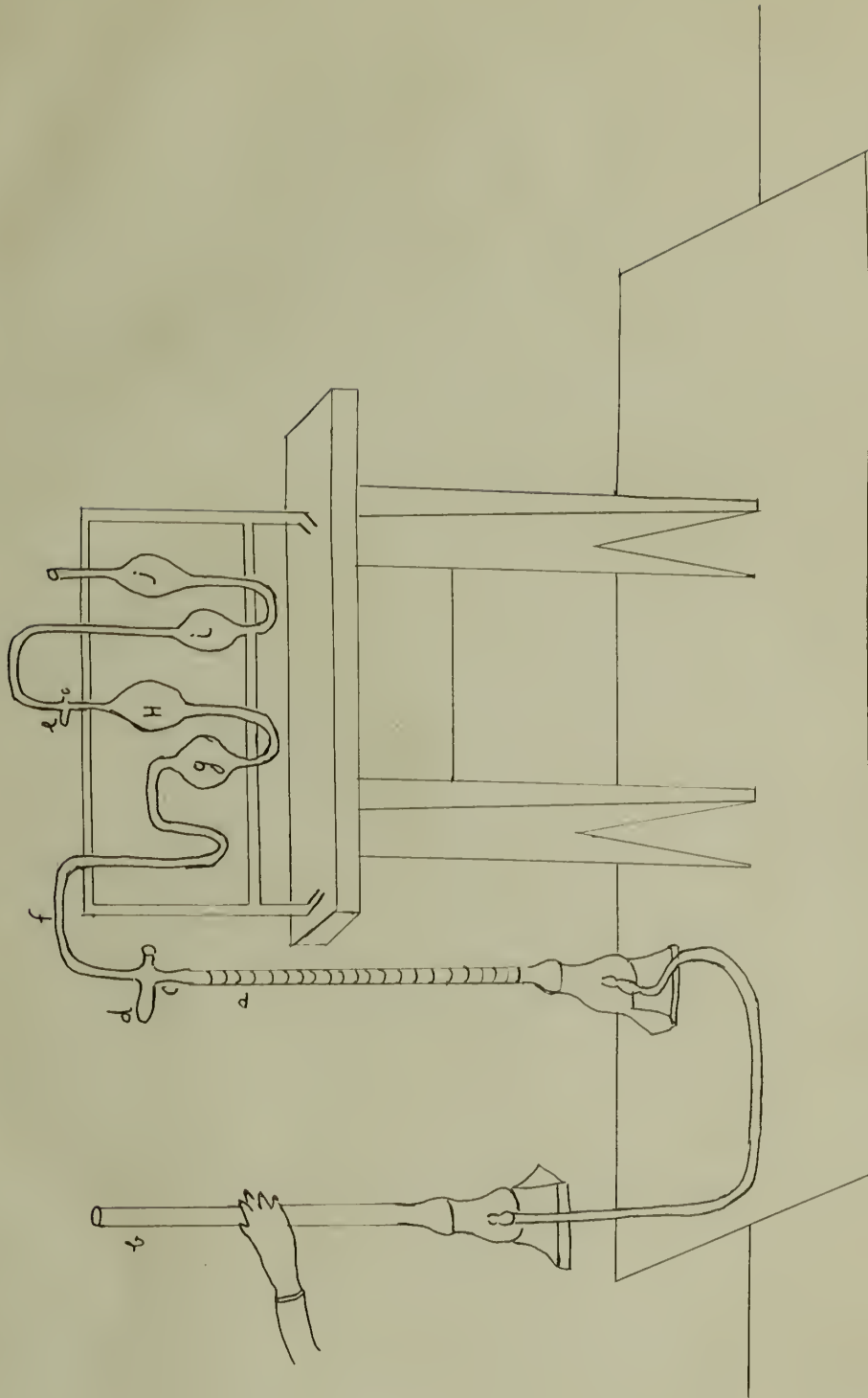
APPARATUS FOR ABSORPTION EXPERIMENTS.

ed supply of air for definite periods of time. The temperature
was kept constant throughout each experiment. Approximately,
50 cc. of air was employed in each case. The dilutions were
exposed to the air and shaken for two minute intervals for the
first ten minutes; then they were shaken for four minute inter-
vals until fifty minutes was reached. It was found that in
most cases fifty minutes was sufficient to absorb all the oxygen
in 50 cc. of air. At the end of each interval, the air was
drawn back into the gas burette and measured. The different
dilutions subjected to this treatment were as follows:

Lime-sulphur solution diluted				1 to 8 Volumes of water				
"	"	"	"	1 " 11	"	"	"	
"	"	"	"	1 " 40	"	"	"	
"	"	"	"	1 " 80	"	"	"	
"	"	"	"	1 " 100	"	"	"	
"	"	"	"	1 " 200	"	"	"	
"	"	"	"	1 " 400	"	"	"	
"	"	"	"	1 " 600	"	"	"	
"	"	"	"	1 " 1000	"	"	"	
"	"	"	"	1 " 2000	"	"	"	
"	"	"	"	1 " 4000	"	"	"	

The numerical data on this series of experiments may be
seen in Tables 1, 2, and 3. The columns of figures show the
decrease in the volume of air as the time of exposure progress-
es. This loss, of course, is due to the oxygen taken up by the
lime-sulphur. It may be clearly seen from these columns of
figures that the absorption of oxygen from the air by the lime-
sulphur proceeds at a definite rate. The rate of absorption

can best be shown from the curves plotted on charts 1 and 2.
If the lime-sulphur solution took up the same amount of oxygen
during equal intervals of time, the curve would become a
straight line. This does not take place, for in all of the
dilutions there is a definite decreasing curve during the fifty
minutes exposure. In all of the dilutions the rate of oxida-
tion tends to be greatest during the first ten minutes. The
curves indicate this by being the straightest during that
period of time.

The dilution 1 to 1 produces the quickest rate of oxida-
tion. This is due to the fact that relatively not much of the
material is oxidized during the time of exposure to the limit-
ed amount of air. At the end of each four minute interval of
exposure, the concentration of such a dilution is not material-
ly changed, and consequently during the next four minute period
it has practically the same ability to unite with oxygen as in
the preceding interval of time. Naturally, as the supply of
oxygen becomes exhausted in the air, the lime-sulphur, no
matter how strong it is, will be unable to secure as much as
it previously did, and that is the reason for the gradual de-
crease in the curve. Although it appears that the surface of
oxygen exposed to the lime-sulphur is the limiting factor when
the oxygen supply is greatly reduced, nevertheless, it is the
surface of the lime-sulphur, which is the controlling factor
in the rate of oxidation.

Concentrations varying from 1 to 1 up to 1 to 2000 bring
out the same facts, and the curves for their rates of oxida-
tion under the above conditions are almost identical. Dilu-

tions from 200 to 1000 also show similar tendencies but as
they become weaker, there is less oxidizable material present,
and consequently the rate of oxidation is somewhat slower.

The most surprising fact which these charts show, is
that on the whole, there is practically little difference be-
tween the rate of oxidation of a very concentrated solution and
of a very dilute solution. There is, in fact, a slower absorp-
tion of oxygen in the weak solutions, but the closeness of the
curves indicate that this difference is almost negligible.
This holds for dilutions from 1 to 1 up to 1 to a 1000. Fur-
ther dilutions, such as 1 to 2000, and 1 to 4000 do proceed
at a slower rate, and do not require nearly so much time for
complete oxidation. For instance, the solution diluted 1 to
2000 was completely oxidized at the end of thirty-four minutes,
and the solution diluted 1 to 4000 at the end of fourteen
minutes. Curves (G) and (H) are the respective curves for
these dilutions. Curve (G) drops quite rapidly during the
first twelve minutes, showing the greatest oxidation. Then the
curve bends gradually, and finally becomes a straight line after
thirty four minutes. Curve (H) descends rapidly for four min-
utes, bends gradually, and finally becomes a straight line after
fourteen minutes. The straight line indicates that the oxida-
tion has given out because all the lime-sulphur is oxidized.
However, as long as there is appreciable material present, the
curves show that the rate of oxidation is much the same, whether
the solution is concentrated or dilute.

Studying the curves of this series as a whole, it will be
noticed that there is a constant rate of oxidation at all dilu-

tions. This fact raises the possibility of the rate of oxi-
dation being directly due to the concentration of the active
parts, ions, which are available to be oxidized. There may be
some buffer action in the mixture which produces a constant
concentration of ions. It seems quite reasonable that the re-
lationship between the ionized and unionized material might
have considerable influence on the rate of oxidation. *

My conclusions upon this first series of experiments
are:

1.   The oxidation of lime-sulphur solutions takes place
at a definite rate.

2.   The rate of oxidation is greatest during the first
ten minutes of exposure and then gradually decreases.

3.   Although there tends to be a slower absorption of
oxygen in weak solutions, on the whole, there is practically
little difference between the rate of oxidation of a very con-
centrated solution and a dilute solution.

4.   The controlling factor in the rate of oxidation is
the amount of surface of lime-sulphur exposed, rather than the
surface of oxygen exposed to lime-sulphur, although the latter
factor seems to be in evidence when the oxygen concentration is
greatly reduced.

* This hypothesis was suggested by Dr. Peters.

TABLE   1.*

CONC. OF LIME-SULPHUR VARIED; TEMP. CONSTANT;VOL. OF AIR LIMITED

Minutes Exposed	Conc.L.S. 1-1 Temp. "27.5°C. " Room "	Conc.L.S. 1-8 Temp." 25°C. " Room "	Conc.L.S. 1-11 Temp. "24°C. " Room ..	Conc.L.S.1-40 Temp."21.5°C. " Room ..
	Figures below are cc. of Air.			
0	49.10	50.20	51.20	50.20
2	47.90	49.10	50.10	48.90
4	47.00	48.10	49.20	48.00
6	46.30	47.10	48.30	47.10
8	45.60	46.20	47.50	46.30
10	45.00	45.50	46.70	45.50
14	43.90	44.20	45.65	44.20
18	42.90	43.20	44.60	43.30
22	42.20	42.50	43.80	42.65
26	41.60	41.90	43.20	42.10
30	41.20	41.40	42.75	41.70
34	40.80	41.00	42.30	41.35
38	40.50	40.60	41.95	41.00
42	40.10	40.40	41.60	40.65
46	39.90	40.30	41.40	
50	39.70	40.20	41.30	

*The abbreviation L.S. stands for lime-sulphur.

TABLE 2.

CONC. OF LIME-SULPHUR VARIED; TEMP. CONSTANT;VOL. OF AIR LIMITED

Minutes Exposed	Conc.L.S. 1-80 Temp. " 22°C. " Room	Conc.L.S.1-100 Temp. " 22°C. " Room	Conc.L.S.1-200 Temp. " 23°C. " Room "	Conc.L.S.1-400 Temp. " 22°C. " Room "
		Figures below are cc. of air.		
0	50.00	49.80	50.00	50.00
2	49.10	48.80	48.90	49.20
4	48.10	47.80	48.00	48.40
6	47.15	46.85	47.10	47.60
8	46.40	46.05	46.40	46.85
10	45.70	45.37	45.70	46.15
14	44.50	44.20	44.50	45.00
18	43.45	43.20	43.50	44.13
22	42.60	42.45	42.80	43.50
26	41.90	41.70	42.10	42.87
30	41.40	41.15	41.40	42.30
34	40.90	40.75	40.90	41.75
38	40.50	40.35	40.50	41.35
42	40.25	40.10	40.30	41.00
46	40.05	39.90	40.10	40.75
50	39.85	39.70	39.90	40.50

TABLE 3.

CONC. OF LIME-SULPHUR VARIED; TEMP. CONSTANT;VOL. OF AIR LIMITED.

Minutes Exposed	Conc.L.S. 1-600 Temp. " 21°C. " Room "	Conc.L.S. 1-1000 Temp. " 22°C. " Room. "	Conc.L.S.1-2000 Temp. " 22 C. " Room "	Conc.L.S.1-4000 Tem. " 24.5°C " Room "
		Figures below are cc. of air.		
0	50.05	50.00	50.00	50.00
2	49.40	49.20	49.20	49.50
4	48.75	48.40	48.60	49.00
6	48.10	47.70	48.10	48.60
8			47.70	48.30
10	46.80	46.60	47.30	48.10
14	45.70	45.50	46.50	48.00
18	44.80	44.50	45.80	48.00
22	44.00	43.80	45.20	48.00
26	43.35	43.20	44.90	48.00
30	42.75	42.70	44.80	48.00
34	42.30	42.20	44.70	48.00
38	41.85	41.90	44.70	48.00
42	41.50	41.60	44.70	48.00
46	41.20	41.40	44.70	48.00
50	41.00	41.20	44.70	48.00

TABLE 3.

CHART 1.

Volume of Air in cc.

Minutes Exposed

A diluted 1 to 1   Temp. 27.5°C. —————   E diluted 1 to 600   Temp. 21°C.
B   "   "   "   25°C. —————   F   "   "   1000   "   22°C.
C   "   "   200   "   23°C. —·—·—   G   "   "   2000   "   22°C.
D   "   "   400   "   22°C. —··—··—   H   "   "   4000   "   24.5°C.

Conc. varied; Temp. constant; Vol. of air limited.

CHART 2.

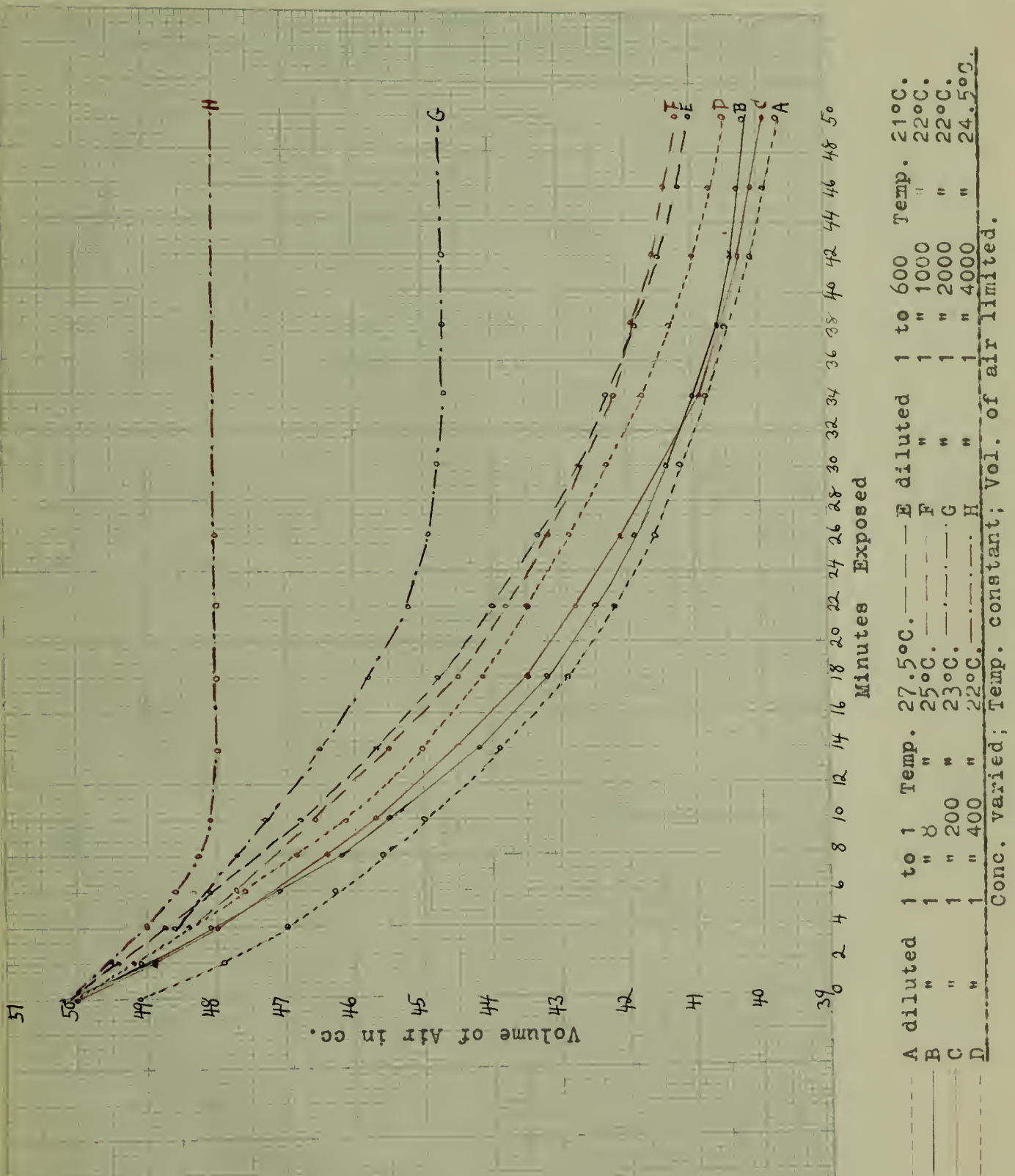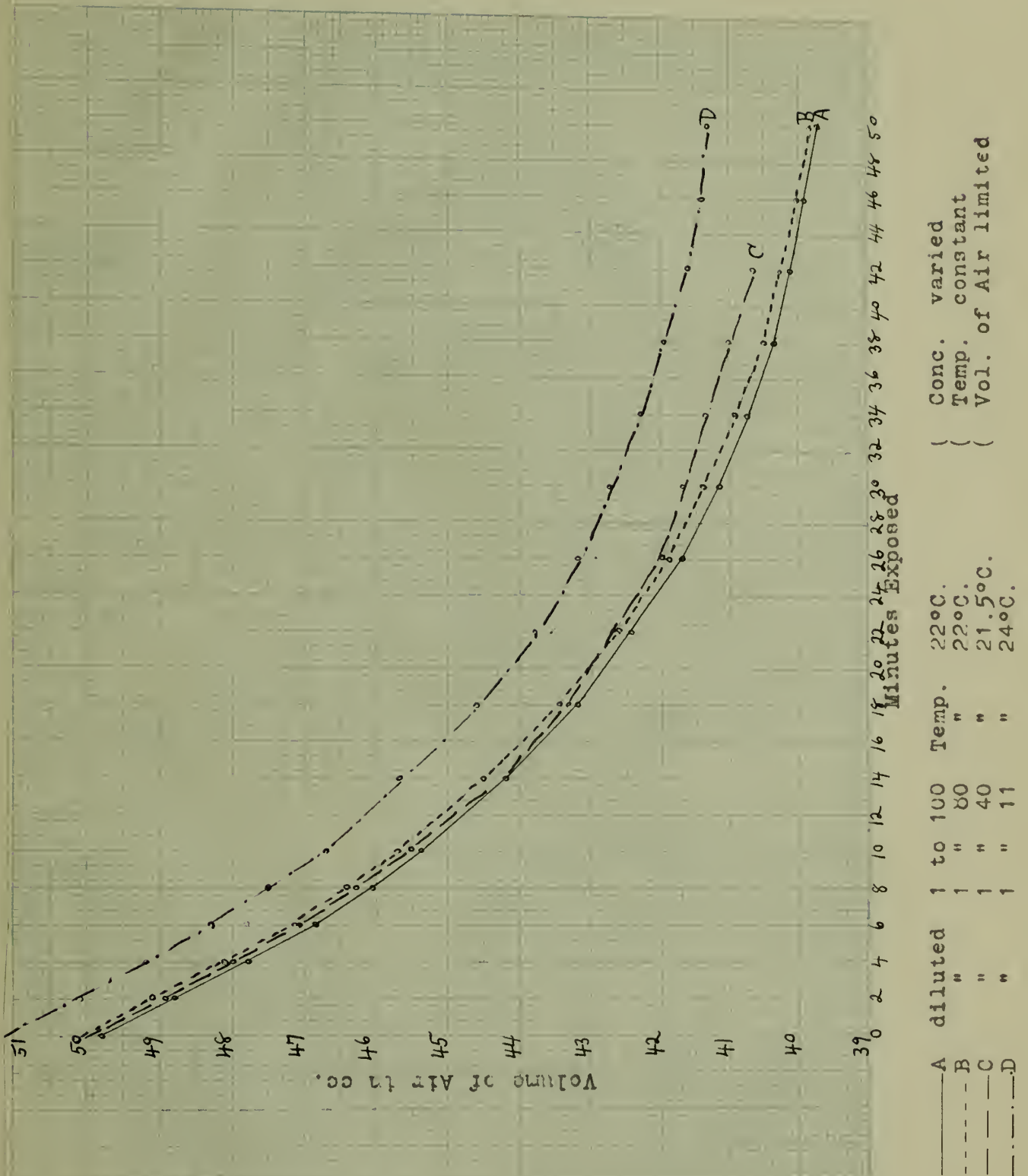|			Temp.		Conc. varied
A	diluted	1 to 100	Temp.	22°C.	Temp. constant
B	"	1 " 80	"	22°C.	Vol. of Air limited
C	"	1 " 40	"	21.5°C.	
D	"	1 " 11	"	24°C.	

Volume of Air in cc.

Minutes Exposed

B.   Concentration of Lime-Sulphur Constant Temperature varied.

In the next series of experiments which were tried, the temperature was varied while the concentration of lime-sulphur and the supply of air were kept constant. The exposure of particular dilutions as represented in the graphs on Charts 3, 4, 5, 6 and 7 for fifty minutes was made separately under four different temperatures: namely, room temperature, (21.5° - 27.5°) 40°C., 60°C., and 80°C.   The same apparatus was used as described except the bulbs (g) and (h) were submerged in a vessel of water which could be heated. The water was stirred and kept at constant temperature. Table 4 and Chart 3 show the results with a dilution of 1 to 1. Here, there is evidently a marked increase in the rate of oxidation as the temperature goes up. Curves (C) and (D), where the temperature is at 60°C,. and 80°C. respectively, show that the oxygen in 50 cc. of air is completely absorbed in thirty minutes time.

Table 5 and Chart 4 show a dilution of 1 to 8 at the four different temperatures. This is the dilution used for the San Jose Scale. The chief fact to be noted here is that curve (A) and (B), which are at room temperature and 40°C. respectively, show very little difference. In fact toward the end, curve (B) tends toward a slower rate of oxidation than curve (A). This fact corroborated in Charts 5 and 6 does away with the possibility of employing heat to increase the efficiency of the lime-sulphur as a spray solution. Curves (C) and (D) (Chart 4), being at considerably higher temperatures, do show a marked increase in the rate of oxidation.

The above facts become more evident in Chart 5 and Table 6, where the dilution is 1 to 40. In fact, there is hardly any difference in the rate of absorption at room temperature, 40°C., and 60°C.

A new condition of affairs appears in Chart 6 and Table 7, where the dilution is 1 to a 100. Here the highest rate of oxidation appears to take place at room temperature as shown by curve (A). At the three other temperatures the curves are much alike with a tendency for the slowest absorption to take place at 40° C. This fact would tend to indicate that the very dilute samples would best oxidize at ordinary room temperature. Further proof of this is shown in Chart 7 and Table 8, where the dilution was 1 to a 1000. Curve (A), which is at room temperature, shows much greater absorbing power for oxygen than curve (B) where the temperature was at 80 °C.

The conclusions which may be drawn from this last series of experiments are as follows:

1. With very concentrated solutions, the increase of temperature causes an appreciable increase in the rate of oxidation.

2. With moderate dilutions, such as 1 to 8 and 1 to 40, the increase in the rate of oxidation is inappreciable up to temperatures of 40°C. and 50°C. Beyond that temperature the rate does increase considerably.

3. For great dilutions, such as 1 to 100 or more, the rate of oxidation is higher at room temperature.

TABLE 4.

CONC. OF LIME-SULPHUR CONSTANT; TEMP. VARIED; VOL. OF AIR LIMITED

Minutes Exposed	Conc.L.S.1-1 Temp. "27.5°C. " Room 27.5°C.	Conc.L.S.1-1 Temp. "40°C. " Room 28°C.	Conc.L.S.1-1 Temp. "60°C. " Room 35°C.	Conc. L.S.1-1 Temp. "80°C. " Room 35°C.
	Figures below are cc. of Air			
0	49.10	50.00	50.00	50.00
2	47.90	48.20	47.20	46.40
4	47.00	46.60	45.20	44.10
6	46.30	45.60	43.80	42.50
8	45.60	44.60	42.80	41.50
10	45.00	43.80	42.00	41.00
14	43.90	42.70	40.90	40.40
18	42.90	42.00	40.40	40.00
22	42.20	41.30	40.00	39.80
26	41.60	40.90	39.80	39.70
30	41.20	40.60	39.70	39.70
34	40.80	40.30	39.70	39.70
38	40.50	40.00	39.70	39.70
42	40.10	39.90	39.70	39.70
46	39.90	39.85	39.70	39.70
50	39.70	39.80	39.70	39.70

CHART 3.

Minutes Exposed

Volume of Air in cc.

A diluted 1 to 1   Temp. of Lime-Sulphur 27.5°C.   Temp. of room 27.5°C.
B "   "   1 " 1   "   " "   "   40°C.   "   "   " 28°C.
C "   "   1 " 1   "   " "   "   60°C.   "   "   " 35°C.
D "   "   1 " 1   "   " "   "   80°C.   "   "   " 35°C.

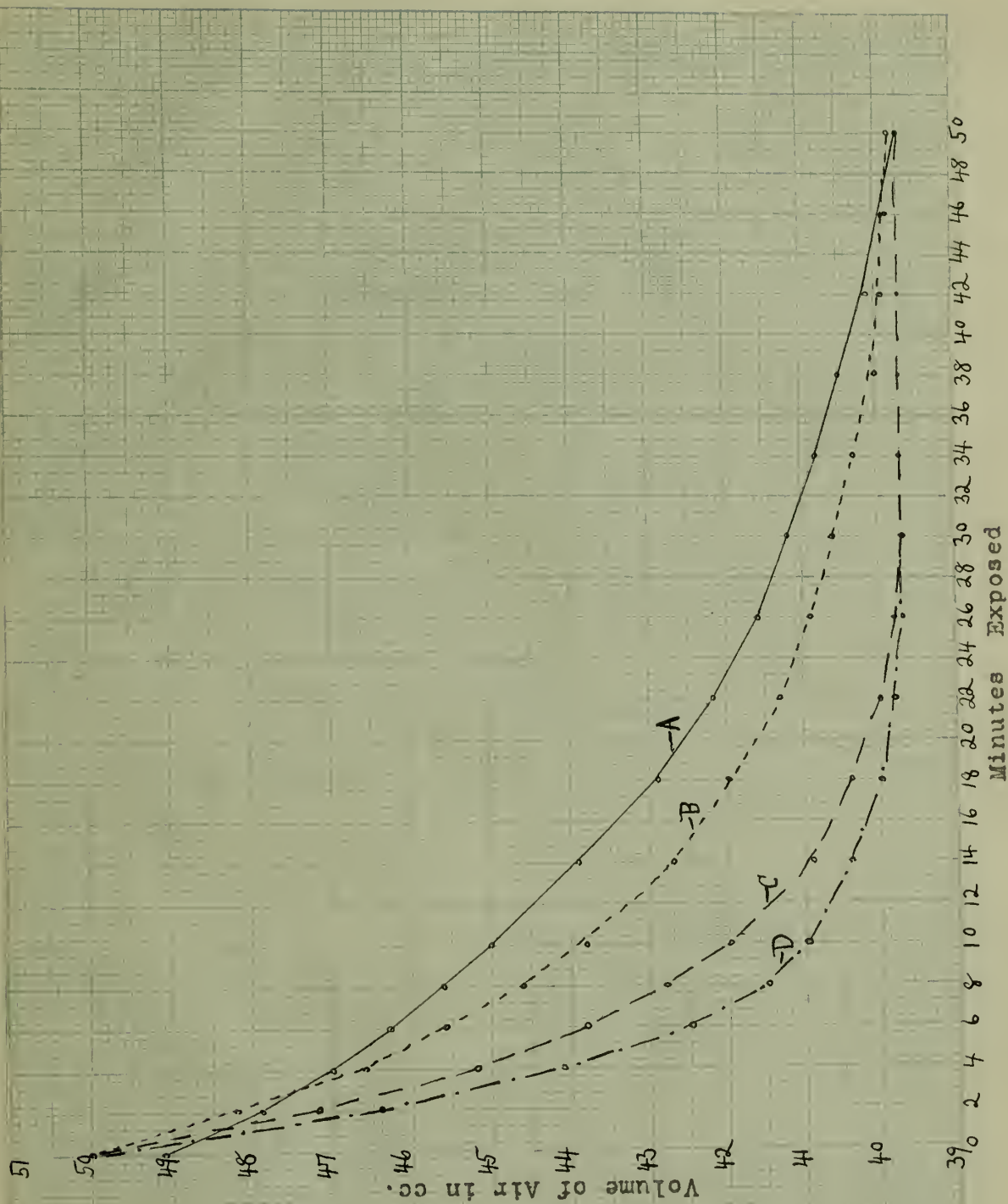Conc. constant; Temp. varied; Vol. of Air limited.

TABLE 5

CONC. OF LIME-SULPHUR CONSTANT; TEMP. VARIED; VOL. OF AIR LIMITED

Minutes Exposed	Conc.L.S.1-8 Temp. "25°C. "Room 25°C.	Conc.L.S.1-8 Temp. "40°C. " Room 23°C.	Conc.L.S.1-8 Temp. "60°C. "Room 23°C.	Conc.L.S.1-8 Temp. "80°C. "Room 27°C.
Figures below are cc. of Air				
0	50.20	50.00	50.00	50.00
2	49.10	48.80	48.20	47.30
4	48.10	47.70	46.80	45.10
6	47.10	46.80	45.50	43.70
8	46.20	46.00		42.80
10	45.50	45.40	43.80	42.00
14	44.20	44.40	42.80	41.00
18	43.20	43.50	41.80	40.60
22	42.50	42.90	41.40	40.35
26	41.90	42.30	41.10	40.10
30	41.40	41.90	40.80	40.00
34	41.00	41.50	40.70	40.00
38	40.60	41.10	40.60	40.00
42	40.40	40.70	40.50	40.00
46	40.30	40.50	40.50	40.00
50	40.20	40.30	40.50	40.00

CHART 4

Minutes Exposed

Volume of Air in cc.

A diluted 1 to 8   Temp. of Lime-Sulphur 25°C.   Temp. of room 25°C.
B   "   "   1 " 8   "   "   "   40°C.   "   "   "   23°C.
C   "   "   1 " 8   "   "   "   60°C.   "   "   "   23°C.
D   "   "   1 " 8   "   "   "   80°C.   "   "   "   27°C.

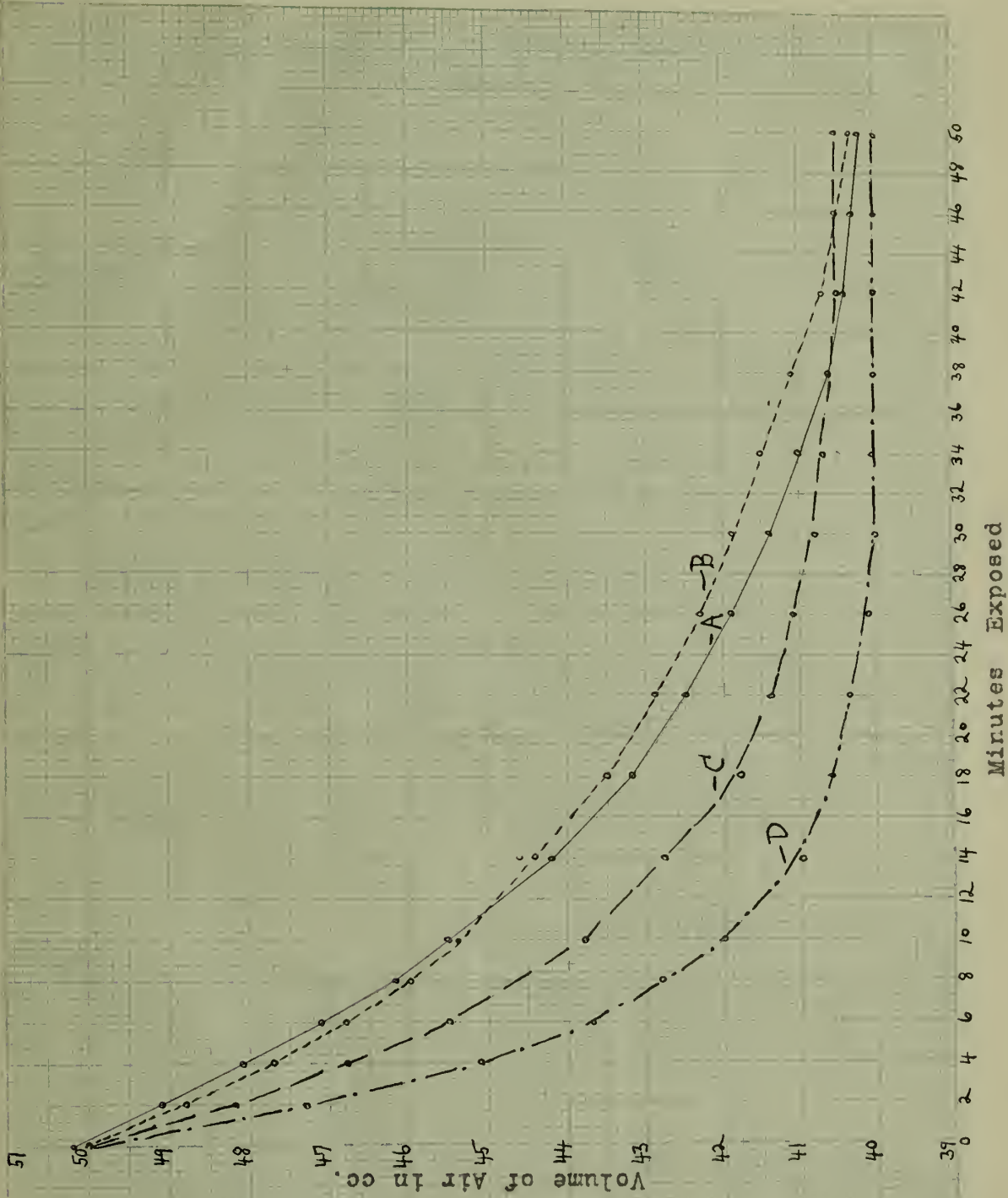Conc. constant; Temp. varied; Vol. of Air limited.

TABLE 6.

CONC. OF LIME-SULPHUR CONSTANT; TEMP. VARIED; VOL. OF AIR LIMITED

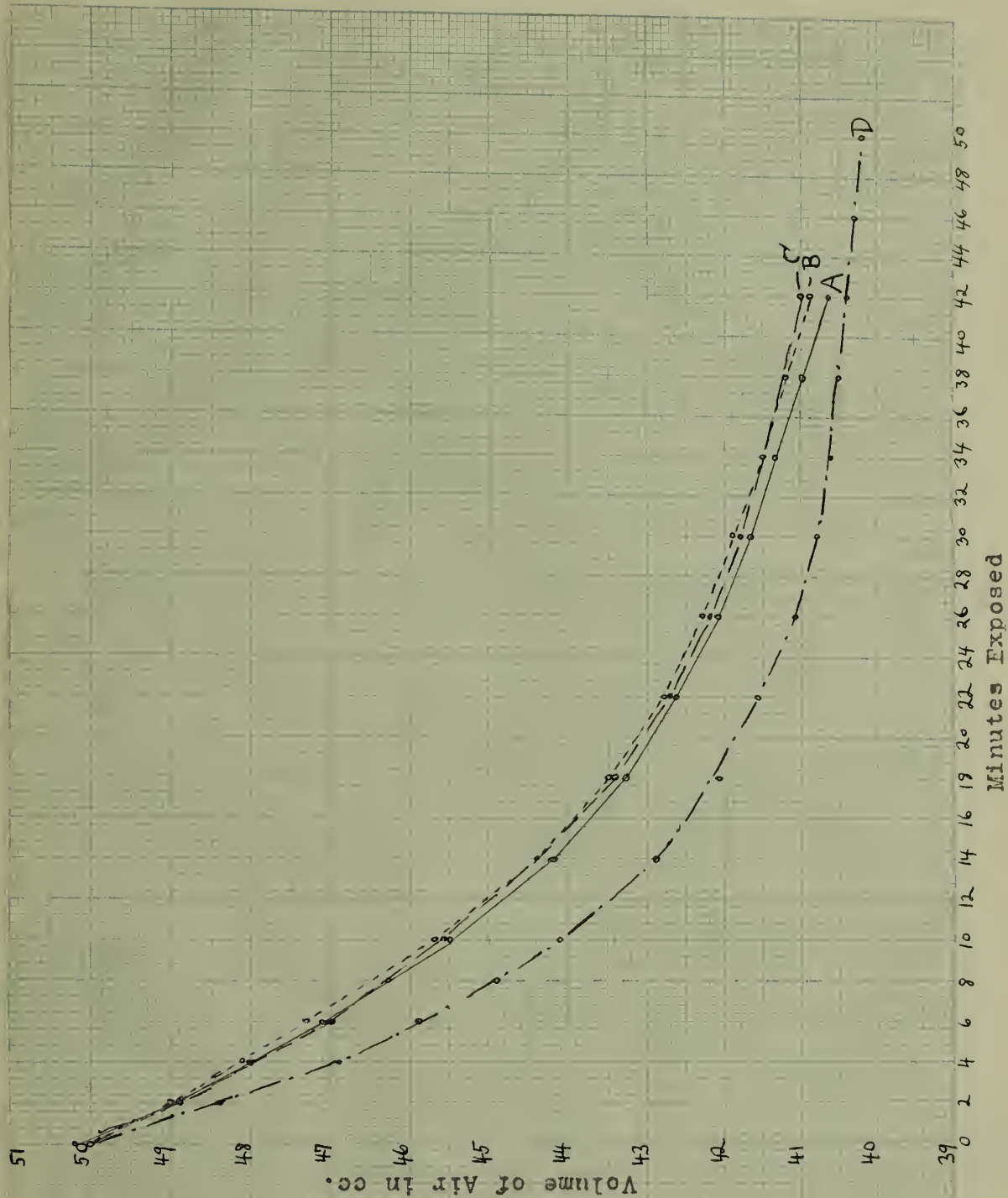| Minutes Exposed	Conc.L.S.1-40 Temp. "21.5° C. "Room 21.5°C.	Conc.L.S.1-40 Temp. "40°C. " Room 22°C.	ConcL.S.1-40 Temp. " 60°C. " Room 24°C.	Conc.L.S.1-40 Temp. " 80°C. " Room 26°C.
	Figures below are cc of Air			
0	50.20	50000	50.00	50.00
2	48.90	48.90	49.00	48.40
4	48.00	48.10	48.00	46.90
6	47.10	47.30	47:00	45.90
8	46.30	——	——	44.90
10	45.50	45.70	45.60	44.10
14	44.20	44.40	44.40	42.90
18	43.30	43.50	43.40	42.10
22	42.65	42.80	42.70	41.60
26	42.10	42.30	42.20	41.10
30	41.70	41.90	41.80	40.80
34	41.35	41.50	41.50	40.60
38	41.00	41.20	41.20	40.50
42	40.65	40.90	41.00	40.40
46				40.30
50				40.20

CHART 5.

TABLE 7.

CONC. OF LIME-SULPHUR CONSTANT; TEMP. VARIED; VOL. OF AIR LIMITED

Minutes Exposed	Conc.L.S.1-100 Temp. "22°C. " Room 22°C.	Conc.L.S. 1-100 Temp. " 40°C. " Room 26°C.	Conc.L.S.1-100 Temp. " 60°C " Room 29.5°C	Conc.L.S.1-100 Temp. " 80°C. " Room 34°C.
	Figures below are cc of Air			
0	49.80	50.00	50.00	50.00
2	48.80	49.50	49.40	49.30
4	47.80	49.00	48.60	48.50
6	46.85	48.40	47.90	47.60
8	46.05	47.80	47.20	46.90
10	45.37	47.20	46.50	46.30
14	44.20	46.00	45.50	45.30
18	43.20	45.10	44.80	44.30
22	42.45	44.30	44.10	43.60
26	41.70	43.60	43.40	43.00
30	41.15	43.00	42.80	42.50
34	40.75	42.50	42.30	42.10
38	40.35	42.00	41.90	41.70
42	40.10	41.60	41.50	41.40
46	39.90	41.20	41.20	41.10
50	39.70	40.90	40.90	40.80

CHART 6.

Minutes Exposed

Volume of Air in cc.

A diluted	1 to 100	Temp. of Lime-Sulphur 22°C.	Temp. of room 22°C.
B "	1 " 100	" " " 40°C.	" " " 26°C.
C "	1 " 100	" " " 60°C.	" " " 29.5°C.
D "	1 " 100	" " " 80°C.	" " " 34°C.

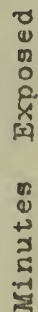Conc. constant; Temp. varied; Vol. of Air limited.

TABLE 8.

CONC. OF LIME-SULPHUR CONSTANT; TEMP. VARIED; VOL. OF AIR LIMITED

Minutes Exposed	Conc. L.S.1-1000 Temp. " 22 °C. " Room 22 °C.	Conc.L.S.1-1000 Temp. " 80 °C. " Room 35 °C.
	Figures below are cc of Air	
0	50.00	50.00
2	49.20	49.50
4	48.40	49.00
6	47.70	48.60
8		48.20
10	46.60	47.80
14	45.50	47.10
18	44.50	46.40
22	43.80	45.80
26	43.20	45.30
30	42.70	44.90
34	42.20	44.50
38	41.90	44.20
42	41.60	43.90
46	41.40	43.70
50	41.20	43.50

CHART 7.

Minutes Exposed

Volume of Air in cc.
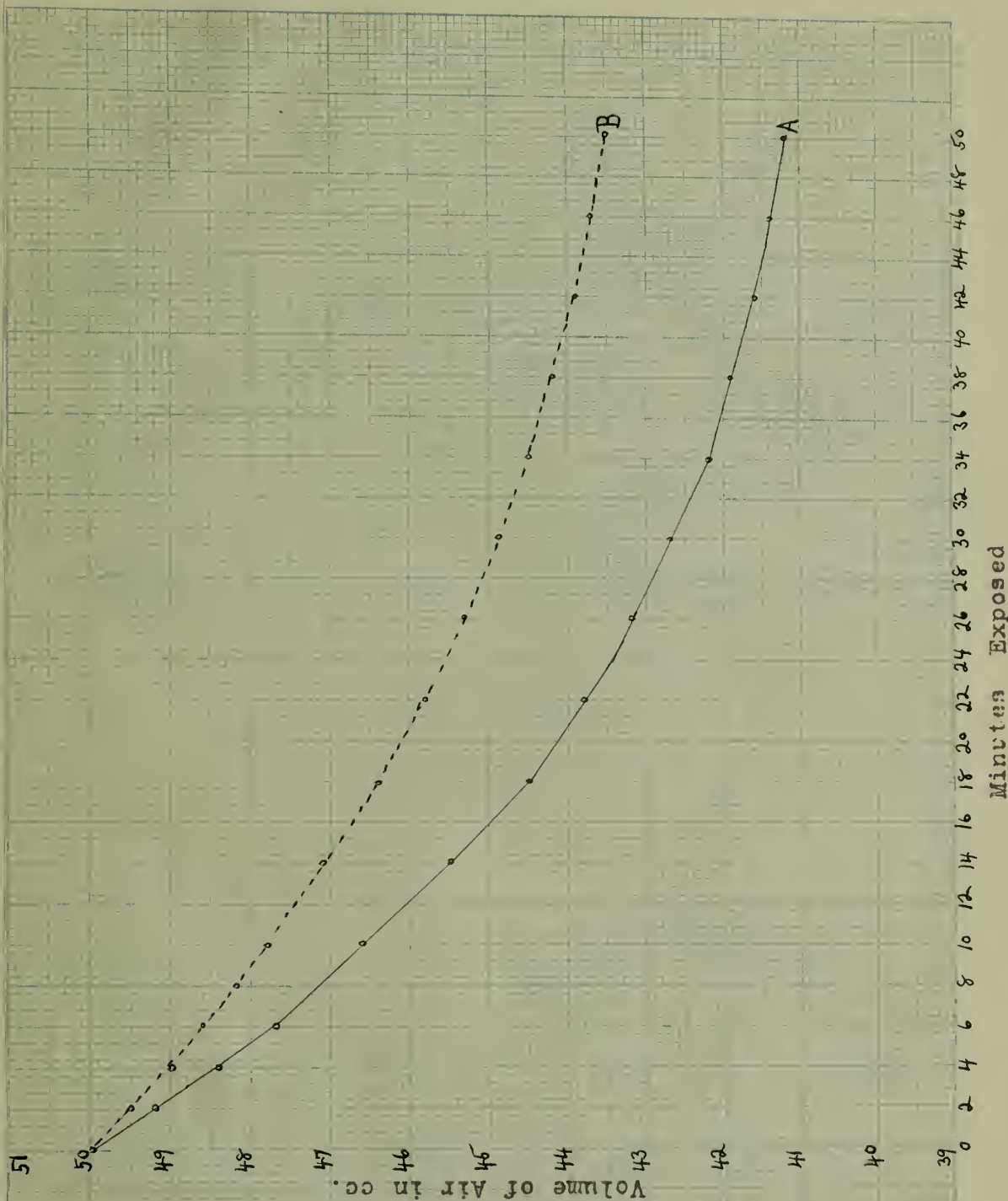
A diluted 1 to 1000   Temp. of Lime-Sulphur 22°C.   Temp. of room 22°C.
B   "   1 " 1000   "   "   "   80°C.   "   "   "   35°C.

———— Conc. constant; Temp. varied; Vol. of Air limited.

Part 2.   Experiments in an Unlimited Supply of Air.

The next step in the problem was to determine the rate
of oxidation when an unlimited supply of air was employed.   To
study the problem from this angle, a different method of pro-
cedure was necessary.   The absorption apparatus could not be
used.   To analyze the material for thiosulphate at definite in-
tervals of time after exposing the solution to the air, seemed
to be the best method to adopt, as the thiosulphate is produced
by oxidation.   The polysulphides of the material react with the
oxygen of the air to first form thiosulphate and free sulphur.

$$CaS_5 \text{ plus } 30 = CaS_2O_3 \text{ plus } 3S$$

The thiosulphate produced can then be readily determined by
means of standard iodine solution.   The amount of thiosulphate
will depend upon the surface, and length of time the material
is exposed to the air.   Hence, there is no reason why the measure
of the thiosulphate should not be the measure of the oxidation.
About 800 cc. of a 1 to 8 lime-sulphur solution was put in a
large shallow dish.   A mechanical glass stirrer, run by water
power from the faucet was introduced into the lime-sulphur solu-
tion.   At intervals of four minutes, 10 cc. of the solution was
removed and anlayzed for thiosulphates.   The results of the
analysis are shown in Table 9, and are entirely unsatisfactory.
Although there is a general tendency toward an increased amount
of thiosulphate being produced, the results are so variable that
they are of little value.   The oxidation by this method increased
the percent of thiosulphate sulphur from 3.40 to 3.85, an increase
of 0.65, whereas a complete oxidation would have raised the figure

to 22-25%. The inconsistencies, no doubt, were due to faults in the apparatus, which probably did not allow the material to be evenly exposed to the air. It was evident that the material would have to be exposed evenly to a much larger volume of air in order to obtain a greater oxidation necessary to measure the rate.

TABLE 9.

CONC. OF LIME-SULPHUR 1-3; VOL. OF AIR UNLIMITED; TEMP. OF ROOM 28 °C.

(800 cc. of material used and constantly stirred)

MINUTES EXPOSED	THIOSULPHATE FIGURE	PER CENT THIOSULPHATE
0	5.30	3.40
4	5.30	3.40
8	5.50	3.53
12	5.40	3.46
16	5.30	3.40
20	X	X
24	5.20	3.37
26	5.60	3.59
32	5.00	3.21
36	5.30	3.40
40	5.80	3.72
44	5.60	3.59
50	5.90	3.78
2 hours	6.00	3.85

Work on the problem was interrupted at this stage (June 21, 1919) and was not resumed again until the fall and winter of 1919

and 1920. As the writer was then working at the New Jersey Experiment Station, a new sample of lime-sulphur had to be obtained and analysed. The analysis was made according to the methods of Chapin described previously. The result of the analysis was as follows:

Specific Gravity	Thiosulphate Figure	Per cent Thiosulphate Sulphur	Reaction Figure	Sulphide acid Figure	Sulphide base Figure	Per cent Monosulphide Sulphur	Polysulphide Figure	Per cent Polysulphide Sulphur
1.32 or 35.3Be	1.1	0.706	-0.25	48.88	48.63	7.84	72.71	23.32

Total Sulphide Sulphur - Per cent	Per Cent Total Sulphur	Total Equivalent CaO*	Analytical Ratio Total CaO / Total S	Value of X in CaS_x
31.16	31.87	14.27	0.448	3.97

* Estimated by calculation from the results for the various forms of sulphur.

From the preceding analysis it was concluded that the
material would be satisfactory to work with. The amount of
thiosulphate sulphur (0.806%) was considerably lower than in
the former sample (2.78%), while the value of X in CaS_x was
3.97 as against 4.65 in the former sample.

New Apparatus

A new form of apparatus for drawing air through the lime-
sulphur solution was devised and tried out. It consisted of an
inverted bell jar placed high on the wall to
serve as a reservoir into which water flowed
from the faucet by means of connecting tub-
ing. A siphon was put into the reservoir and
connected at about the neck of the bell jar
with an inverted funnel shaped tube such as
is frequently used to hold a Gooch filter.
The funnel contained a two-hole stopper.
Through one hole a large glass tube was in-
serted to carry off the siphon water. Through
the other hole was placed a glass u-bent tube,
and connected to a 250 cc. gas collecting
bottle at a lower level, which was to contain
the lime-sulphur solution. A glass tube hav-
ing a perforated bulb on one end, dipped be-
low the solution, and served as the entrance
for the air when the siphon was running. This
apparatus which is shown in the accompanying
diagram, functions as a water pump, and hence could be used to
draw air through the lime-sulphur solution. The bottle which
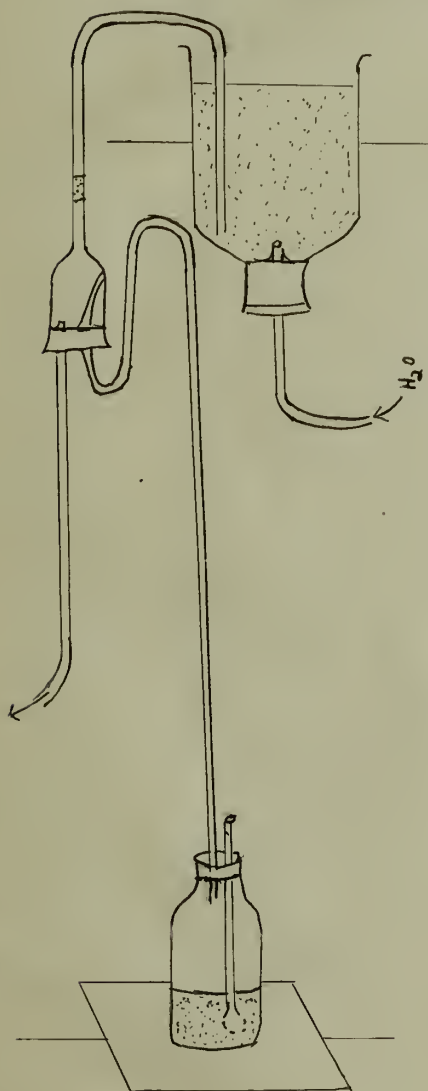
held the lime-sulphur solution had a depth of 12 cm., a diameter
of 5 cm., and a capacity of 250 cc.   The diameter of the tube
through which the air came in was 7 mm.   The bulb of this in-
let tube had four holes in it, with an approximate diameter of
2 mm. each.   The amount of water flowing through the apparatus
was 1100 cc. per minute.

A definite volume (100 cc.) of 1 to 10 lime-sulphur solu-
tion was introduced into the bottle and air drawn through it for
fifteen minute intervals.   At the end of fifteen minutes the
sample was removed and analyzed for thiosulphates, and a new
sample of the same dilution was replaced and air drawn through
for thirty minutes.   This process was repeated, changing the
samples at the proper intervals, until air had been drawn through
a sample for two hours.   By introducing a new sample at the end
of each period, the volume was kept constant throughout.   After
this treatment, each of the samples were analyzed for the thio-
sulphate figure, from which the per cent of thiosulphate (S in
$Na_2S_2O_3$) was calculated.   Both figures are given in Table 10.
The experiment was repeated using a dilution of 1 to 40, and
1 to 100.   The data for these experiments are given in Tables
10 and 11 and their corresponding curves on Chart 8.

With the 1 to 10 dilution there is a steady increase in
the oxidation as the period of exposure to the air is lengthen-
ed.   The rate appears to be a little irregular, but the general
tendency is apparent.   If anything, the rate of oxidation is
greater during the first forty-five minutes, and then slows
down somewhat.   With dilutions 1 to 40, and 1 to 100, the fig-
ures and curves also show a similarity to the 1 to 10 dilution,

47.

except that the irregularities are not so great. Also it appears more evident with these dilutions that the rate of oxidation is greater during the first hour and then gradually slows down. The partial diminution in the rate of oxidation in all of these dilutions seems to start at about the same point: namely, at the end of the sixty minute period. The slight break in the curves at this point substantiates this view. The rate of oxidation seems to be largely independent of the concentration of the lime-sulphur, although there seems to be a slight decrease with the more dilute solutions as the oxidation progresses. This conclusion agrees with that observed in the first series of experiments.

In Table 11 under dilution 1 to 100, it will be seen that the oxidation of the entire 100 cc. was complete at the end of 105 minutes, for there was no change in the amount of thiosulphate produced by exposing the material for a longer period. Consequently, if the solution were ten times as strong (as was the case with the 1 to 10 solution) it would take theoretically ten times as long, or 1050 minutes, to oxidize it completely, provided the rates of oxidation were the same. In order to test this hypothesis, 100 cc. of dilution 1 to 10 was run to complete oxidation with the above apparatus. It took a period of eighteen hours or 1080 minutes, which checks the results obtained with the 1 to 100 dilution, and shows that the rates of oxidation with the dilutions 1 to 10 and 1 to 100 to be same, verifying the data shown in Table 11.

The data obtained in these experiments are, of course, arbitrary being dependent entirely on the apparatus employed.

If the apparatus used were larger or smaller, and the volume
of air drawn through greater or less, a different set of figures
would be obtained, but the relationship should be similar, pro-
viding that the volume of air admitted is kept constant through-
out the experiment.   In order to learn if this were true, the
apparatus was doubled.   Two siphons and two entrance tubes were
used, so that twice the volume of air was drawn through the
lime-sulphur.   Table 11, and Chart 8 furnish the results.   As
would be expected the amount of oxidation is similar to that
where only half the air was employed.   That the rate of oxida-
tion is somewhat more rapid at the beginning, is decidedly more
evident in this experiment than in the previous ones.

TABLE 10.

Dilution 1 to 10

Minutes Exposed	Thiosulphate Figure	Per Cent Thiosulphate
0	1.10	0.74
15	1.66	1.07
30	1.99	1.28
45	2.49	1.60
60	2.69	1.73
75	3.19	2.04
90	3.49	2.24
105	3.69	2.37
120	4.19	2.69
1080 or 18 hrs.	21.88	14.01

Dilution 1 to 40

Minutes Exposed	Thiosulphate Figure	Per Cent Thiosulphate
0	0.35	0.22
15	0.74	0.48
30	1.20	0.77
45	1.60	1.02
60	1.94	1.25
75	2.10	1.35
90	2.40	1.54
105	2.70	1.73
120	2.99	1.93

TABLE   11.

Dilution   1   to   100

Minutes Exposed	Thiosulphate Figure	Per Cent Thiosulphate
0	0.11	0.07
15	0.59	0.38
30	0.87	0.56
45	1.20	0.77
60	1.50	0.96
75	1.70	1.09
90	1.79	1.15
105	1.89	1.22
120	1.89	1.22

Double Apparatus

Dilution   1   to   10

0	1.10	0.74
15	1.89	1.22
30	2.40	1.54
45	2.80	1.80
60	3.19	2.05
75	3.54	2.27
90	3.89	2.50
105	4.24	2.72
120	4.59	2.95

CHART 9.

Minutes Exposed

A diluted 1 to 10
B " 1 " 40
C . " 1 " 100
D " 1 " 10 (double apparatus)

Per Cent Thiosulphate

Part 3.   Oxidation Experiments with Lime-Sulphur in the form
of Spray.

        One other phase of the subject was studied to a slight
extend:namely, to learn to what degree the lime-sulphur was
oxidized while passing through the air as a spray. To deter-
mine this, an ordinary throat atomizer, holding about 40 cc.
of liquid, and producing a very fine spray was used. A piece
of plate glass about twelve inches square and chemically clean,
so that a film of water would run off without leaving any drop-
lets was set up over a dish containing a solution of ammonical
zinc chloride. The lime-sulphur solution of the proper dilu-
tion was then sprayed from the atomizer onto the plate glass.
Most of the spray fell well within an inch of the edge of the
plate. The glass being wet with a film of water caused the
spray to flow down immediately into the ammonical zinc chloride
solution. The latter removed the sulphides, and then the amounts
of thiosulphate which measure the degree of oxidation, were de-
termined as outlined previously. This procedure was carried out
with dilutions 1 to 10, 1 to 40 and 1 to 100.   In all cases, the
surprising fact appears that the amount of oxidation is relatively
very small. One would naturally expect that when the material is
in such a finely divided condition, the oxidation would be almost
instantaneous, as the oxygen supply is seemingly unlimited, and
the surface relatively great, but this is not the case. With dilu-
tion 1 to 10, there is an increase of 0.251 % thiosulphate over
the amount present before the material was sprayed. In other
words, the amount of oxidation was about as great as would be ob-
tained by passing air through the liquid for about twelve minutes
using the other apparatus. With the two other dilutions, the in-

creased amount of thiosulphate due to oxidation is also relatively small.

Some of the material, diluted 1 to 10 was then sprayed at a distance of two feet, which was as far as the atomizer would carry. From Table 12, it is seen that the increased per cent of thiosulphate is about double that obtained when the material was sprayed at a distance of one foot. This corresponds to the amount of oxidation obtained by passing air through the liquid for about thirty minutes using the other apparatus. Consequently, the greater the distance through which the spray is carried in the air, the greater will be the oxidation, but nevertheless it is much slower than would be expected. The oxidation is far from being instantaneous.

TABLE   12

Dilution	Distance of Spray from Plate	Thiosulphate Figure		Per cent Thiosulphate	
1 to 1	12"	(1.55		0.99	
		(1.10	(no oxidation)	0.74	
		(0.45	(increase due to oxidation)	0.25	
1 to 40	12"	(0.50		0.32	
		(0.35	(no oxidation)	0.22	
		(0.15	(increase due to oxidation)	0.10	
1 to 100	12"	(0.30		0.19	
		(0.11	(no oxidation)	0.07	
		(0.19	(increase due to oxidation)	0.12	
1 to 10	24"	(1.89		1.22	
		(1.10	(no oxidation)	0.74	
		(0.79	(increase due to oxidation)	0.48	

This data is too meagre to draw substantial conclusions, but it appears that the oxidation of the dilute solutions, 1 to 40, and 1 to 100 are approximately the same. It is also apparent that the increase in the stronger solution (1 to 10), is double that of

the dilute, and that doubling the distance through which the spray passes doubles the amount of oxidation. Even if the oxidation kept up at this rate during actual spraying at a distance of 10 feet, the amount of thiosulphate formation would be comparatively slight, and not equal to more than is found in some sprays, so that most of the oxidation of lime-sulphur must take place on the tree.

CONCLUSIONS.

1. The oxidation of lime-sulphur solutions takes place at a definite rate.

2. The rate of oxidation is greatest during the first ten minutes of exposure and then gradually decreases.

3. Although there tends to be a slower absorption of oxygen in weak solutions, in general, there is practically little difference between the rate of oxidation of a very concentrated solution and a dilute solution.

4. With very concentrated solutions the increase of temperature causes an appreciable increase in the rate of oxidation.

5. With moderate dilutions such as 1 to 8 and 1 to 40, the increase in the rate of oxidation is inappreciable up to a temperature of about 40° c. or 50° c. Beyond that temperature, the rate does increase considerable.

6. For great dilutions such as 1 to 100 or more, the rate of oxidation takes place more rapidly at room temperature.

7. When the amount of air is unlimited there is a tendency for the oxidation to proceed at a somewhat greater rate at the beginning while the solution is concentrated, but in general, the rate is nearly constant throughout the entire oxidation.

8. The amount of oxidation which occurs while the spray is passing through the air is relatively small at short distances but increases considerably by lengthening the distance through which the spray passes.

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